

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-159990

(43)Date of publication of application : 23.06.1995

(51)Int.Cl.

G03F 7/022

H01L 21/027

(21)Application number : 05-338926

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(22)Date of filing : 02.12.1993

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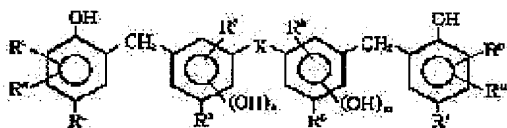
KUSUNOKI TETSUAKI

NAKAMURA MASAHIRO

(54) POSITIVE TYPE RESIST COMPOSITION

(57)Abstract:

PURPOSE: To improve sensitivity, the rate of a residual film, resolution and pattern shape by incorporating alkali-soluble phenolic resin, a specified photosensitive agent and a specified arom. compd.



CONSTITUTION: This resist compsn. contains alkali-soluble phenolic resin, quinonediazidosulfonic ester of a polyhydroxy compd. represented by the formula as a photosensitive agent and an arom. compd. having a phenolic hydroxyl group. In the formula, (k) is 1 or 2, (m) is 1 or 2, each of R1-R4 is halogen, alkyl, alkenyl, alkoxy, aryl or acyl, each of R5-R10 is H, halogen, alkyl,

alkenyl, alkoxy, aryl or acyl, X is a single bond, -O-, -S-, -SO-, -SO2-, -CO-, -CO2-, cyclopentylidene, etc.

LEGAL STATUS

[Date of request for examination] 14.03.2000

[Date of sending the examiner's decision
of rejection]

[Kind of final disposal of application other
than the examiner's decision of rejection
or application converted registration]

[Date of final disposal for application]

[Patent number] 3275505

[Date of registration] 08.02.2002

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against
examiner's decision of rejection]

[Date of extinction of right]

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2.**** shows the word which can not be translated.

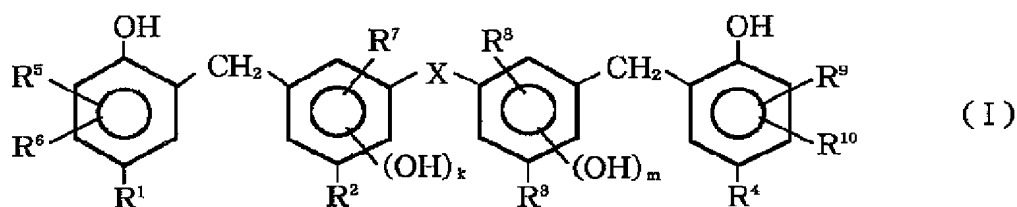
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] (a) The sensitization agent which consists of alkali fusibility phenol resin and
a quinone diazide sulfonate of the polyhydroxy compound expressed with the general
formula (I) of (b) following, and the positive-resist constituent characterized by
containing an aromatic compound with (c) phenol nature hydroxyl.

[Formula 1]



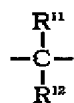
k: — it is 1 or 2.

m: — it is 1 or 2.

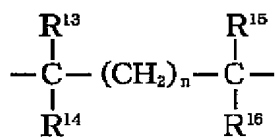
it is R1 — an R4: halogen atom, an alkyl group, an alkenyl radical, an alkoxy group, an aryl group, or an acyl group, and respectively the same — or it may be different from each other.

R5-R10: — it is a hydrogen atom, a halogen atom, an alkyl group, an alkenyl radical, an alkoxy group, an aryl group, or an acyl group, and respectively the same — or it may be different from each other.

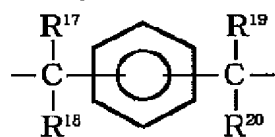
X: Single bond, —O—, —S—, —SO—, —SO2—, —CO—, —CO2—, cyclo pen dust DIN, cyclohexylidene, phenylene, [Formula 2]



(— R11 and R12: — it is a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, or a permutation aryl group, and respectively the same — or it may be different from each other.) — [Formula 3]



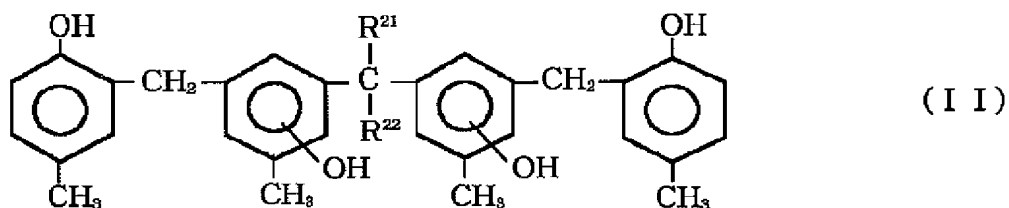
R13-R16: — it is a hydrogen atom or an alkyl group, and respectively the same — or it may be different from each other. n: It is the integer of 1-5. Or [Formula 4]



(— R17-R20: — it is a hydrogen atom or an alkyl group, and respectively the same — or it may be different from each other.) — from — it is the becoming connection radical.

[Claim 2] The positive-resist constituent according to claim 1 whose polyhydroxy compound expressed with a general formula (I) is a compound expressed with the following general formula (II).

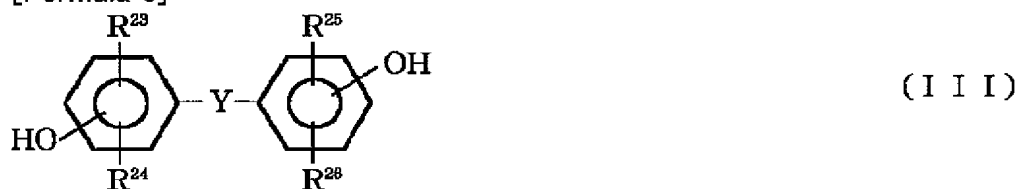
[Formula 5]



R21-R22: -- it is a hydrogen atom or an alkyl group, and respectively the same -- or it may be different from each other.

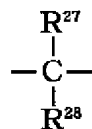
[Claim 3] The positive-resist constituent according to claim 1 whose aromatic compound with phenol nature hydroxyl is an aromatic compound expressed with the following general formula (III).

[Formula 6]

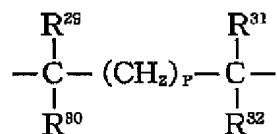


R23-R26: -- it is a hydrogen atom, a halogen atom, hydroxyl, an alkyl group, an alkenyl radical, an aryl group, or an alkoxy group, and respectively the same -- or it may be different from each other.

Y: Single bond, -O-, -S-, -SO-, -SO2-, -CO-, -CO2-, cyclo pen dust DIN, cyclohexylidene, phenylene, [Formula 7]

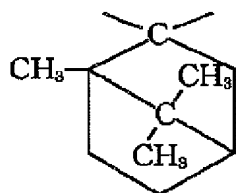


(-- R27 and R28: -- it is a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, or a permutation aryl group, and respectively the same -- or it may be different from each other.) -- [Formula 8]

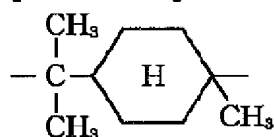


R29-R32: -- it is a hydrogen atom or an alkyl group, and respectively the same -- or it may be different from each other. p: It is the integer of 1-5. [Formula 9]

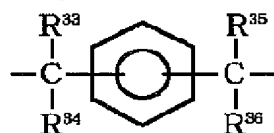
[Formula 10]



[Formula 11]



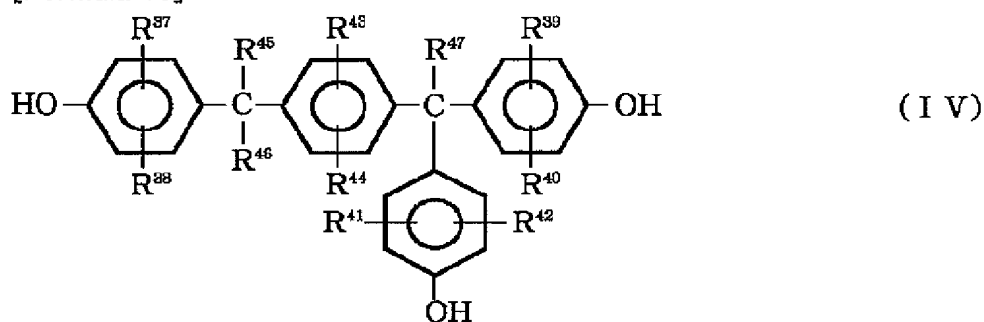
Or [Formula 12]



(-- R33-R36: -- it is a hydrogen atom or an alkyl group, and respectively the same -- or it may be different from each other.) -- from -- it is the becoming connection radical.

[Claim 4] The positive-resist constituent according to claim 1 whose aromatic compound with phenol nature hydroxyl is an aromatic compound expressed with the following general formula (IV).

[Formula 13]

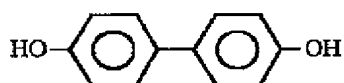


R37-R42: -- it is a hydrogen atom, a halogen atom, hydroxyl, an alkyl group, an alkenyl radical, an aryl group, or an alkoxy group, and respectively the same -- or it may be different from each other.

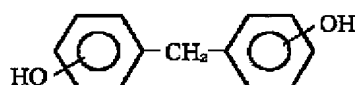
R43 and R44: — it is a hydrogen atom, a halogen atom, or an alkyl group, and respectively the same — or it may be different from each other.

R45-R47: -- it is a hydrogen atom or an alkyl group, and respectively the same -- or it may be different from each other.

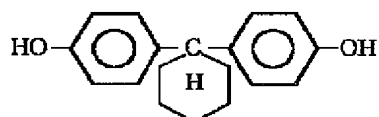
[Claim 5] The aromatic compound expressed with a general formula (III) is [Formula 14].



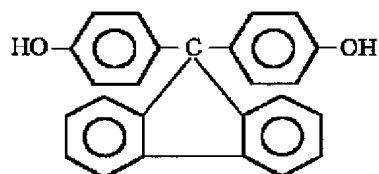
[Formula 15]



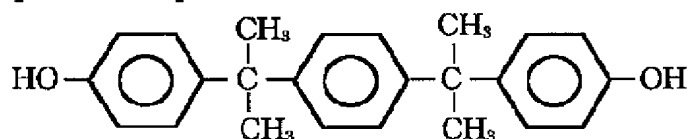
[Formula 16]



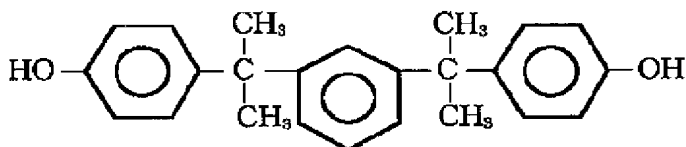
[Formula 17]



[Formula 18]

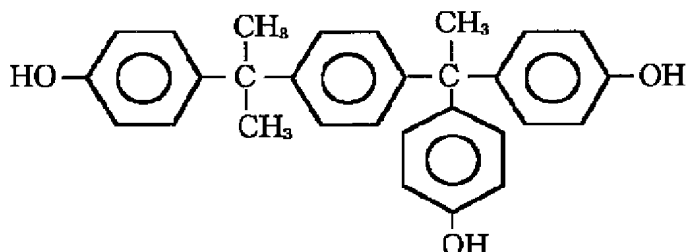


Or [Formula 19]



It comes out and is a certain positive-resist constituent according to claim 3.

[Claim 6] The aromatic compound expressed with a general formula (IV) is [Formula 20].



It comes out and is a certain positive-resist constituent according to claim 4.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the positive-resist constituent for micro processing required for manufacture of a semiconductor device, a magnetic-bubble-memory component, an integrated circuit, etc. in more detail about a positive-resist constituent.

[0002]

[Description of the Prior Art] In order to form a detailed pattern using a resist, after applying the solution containing a photosensitive ingredient (resist constituent), making it dry on a substrate and creating a film, an activity beam of light is irradiated, a latent image is formed, subsequently, negatives are developed and the image of a negative mold or a positive type is created. The resist film is removed, after forming an image (pattern) and usually etching subsequently to a substrate top with the above-mentioned lithography technique by using the resist which remained as a protective coat, using a silicon wafer as a substrate, in order to manufacture a semiconductor device by micro processing using a resist. At a positive resist, the

non-irradiating part of solubility in the inside of a developer of a film increases compared with a non-irradiated part, a positive type image is given, by negative resist, the solubility of the non-irradiating part of a film decreases and a negative-mold image is given.

[0003] as the resist constituent for forming a semiconductor device conventionally -- cyclization -- the negative resist which consists of polyisoprene and a bis-diazido compound is known. However, since this negative resist is developed by the organic solvent, swelling is large and a limitation is in definition, it has the fault which cannot respond to manufacture of the semi-conductor of a high degree of integration. Moreover, although the negative resist containing polymethacrylic acid glycidyl is high sensitivity, it is inferior to resolution or dry etching nature.

[0004] It is thought that it can respond to high integration of a semi-conductor enough to this negative-resist constituent on the other hand since the positive-resist constituent is excellent in definition. The positive-resist constituent generally used in current and this field consists of alkali fusibility resin and quinone diazide compounds, such as novolak resin. This positive-resist constituent can perform development by the alkali water solution, and is excellent in definition. Moreover, by high performance-ization of engine-performance amelioration of itself, and an exposure machine, resolution of a positive-resist constituent [such] improves and the formation of a detailed pattern 1 micrometer or less of it has also been attained.

[0005] However, it is not obtained but much more improvement in the engine performance is desired by the result with the conventional positive-resist constituent not necessarily satisfactory in respect of many properties, such as sensibility, a remaining rate of membrane, resolution, thermal resistance, and preservation stability. Moreover, 1 micrometer or less of things for which the dimension of a resist is controlled more severely is needed in especially detailed pattern formation 0.8 micrometers or less, therefore a positive-resist constituent with more sufficient dimensional accuracy is called for strongly.

[0006] Recently, in the positive resist containing alkali fusibility phenol resin and a sensitization agent, using the quinone diazide sulfonate of various phenolic compounds is proposed as a sensitization agent (for example, JP,2-296248,A, JP,2-296249,A). However, the positive-resist constituent currently indicated concretely has sensibility, resolution, a remaining rate of membrane, or a pattern configuration a little inadequate for these reference, and the further improvement is called for.

[0007]

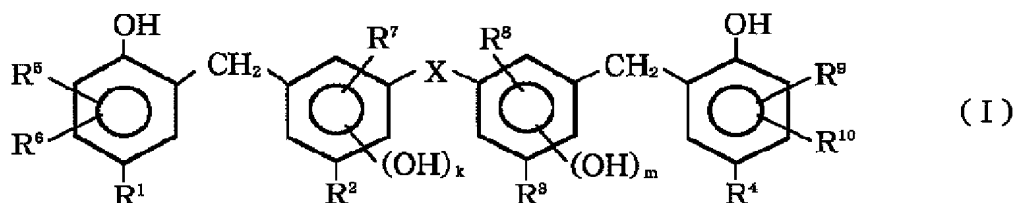
[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer balance ***** of many properties, such as sensibility, a remaining rate of membrane, resolution, and a pattern configuration, and the positive-resist constituent suitable for especially micro processing 1 micrometer or less. this invention persons found out that said purpose could be attained as (a) alkali fusibility phenol resin and a (b) sensitization agent by using the photosensitive ingredient which combined the quinone diazide sulfonate of a specific polyhydroxy compound, and the aromatic compound with (c) phenol nature hydroxyl, as a result of inquiring wholeheartedly, in order to conquer the trouble which said conventional technique has. The balance ***** cage of many properties, such as sensibility, a remaining rate of membrane, resolution, and a pattern configuration, thermal resistance, preservation stability, dry etching-proof nature, etc. are good, the photosensitive ingredient, i.e., the positive-resist constituent, of this invention. This invention comes to be completed based on these knowledge.

[0008]

[Means for Solving the Problem] In this way, according to this invention, the positive-resist constituent characterized by containing the sensitization agent which consists of (a) alkali fusibility phenol resin and a quinone diazide sulfonate of the polyhydroxy compound expressed with the general formula (I) of (b) following, and an aromatic compound with (c) phenol nature hydroxyl is offered.

[0009]

[Formula 21]



k: -- it is 1 or 2.

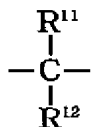
m: -- it is 1 or 2.

it is R1 - an R4: halogen atom, an alkyl group, an alkenyl radical, an alkoxy group, an aryl group, or an acyl group, and respectively the same -- or it may be different from each other.

R5-R10: -- it is a hydrogen atom, a halogen atom, an alkyl group, an alkenyl radical, an alkoxy group, an aryl group, or an acyl group, and respectively the same -- or it may be different from each other.

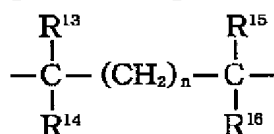
X: Single bond, -O-, -S-, -SO-, -SO₂-, -CO-, -CO₂-, cyclo pen dust DIN, cyclohexylidene, phenylene, [0010]

[Formula 22]



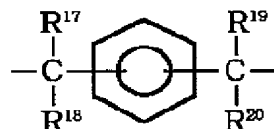
(— R¹¹ and R¹²: — it is a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, or a permutation aryl group, and respectively the same — or it may be different from each other.) — 0011]

[Formula 23]



R¹³-R¹⁶: — it is a hydrogen atom or an alkyl group, and respectively the same — or it may be different from each other. n: It is the integer of 1-5. Or [0012]

[Formula 24]



(— R¹⁷-R²⁰: — it is a hydrogen atom or an alkyl group, and respectively the same — or it may be different from each other.) — from — it is the becoming connection radical.

[0013] Hereafter, this invention is explained in full detail.

(a) As alkali fusibility phenol resin used in alkali fusibility phenol resin this invention, the condensation reaction product of phenols and aldehydes, the condensation reaction product of phenols and ketones, a vinyl phenol system polymer, an isopropenyl phenol system polymer, the hydrogenation resultant of these phenol resin, etc. are mentioned, for example. As an example of the phenols used here, polyhydric phenols, such as the phenols of monovalence, such as a phenol, cresol, a xylenol, ethylphenol, a propyl phenol, butylphenol, and phenylphenol, resorcinol, a pyrocatechol, hydroquinone, bisphenol A, a phloroglucinol, and pyrogallol, are mentioned.

Formaldehyde, an acetaldehyde, a benzaldehyde, a terephthal aldehyde, etc. are mentioned as an example of aldehydes. As an example of ketones, an acetone, a

methyl ethyl ketone, a diethyl ketone, diphenyl ketone, etc. are mentioned. These condensation reactions can be performed according to a conventional method.

[0014] A vinyl phenol system polymer is chosen from the homopolymer of a vinyl phenol, and the copolymer of a vinyl phenol and a copolymerizable component. As an example of a copolymerizable component, an acrylic acid, a methacrylic acid, styrene, a maleic anhydride, maleic-acid imide, vinyl acetate, acrylonitrile, these derivatives, etc. are mentioned. An isopropenyl phenol system polymer is chosen from the homopolymer of an isopropenyl phenol, and the copolymer of an isopropenyl phenol and a copolymerizable component. As an example of a copolymerizable component, an acrylic acid, a methacrylic acid, styrene, a maleic anhydride, maleic-acid imide, vinyl acetate, acrylonitrile, these derivatives, etc. are mentioned. When using the hydrogenation resultant of phenol resin, the product can be manufactured by the well-known approach of arbitration. For example, phenol resin is dissolved in an organic solvent and it can attain by introducing hydrogen under existence of the catalysts for hydrogenation of a homogeneous system or a heterogeneous system.

[0015] Although these alkali fusibility phenol resin is used even when it is independent, two or more sorts may be mixed and used for it. Moreover, although it is used even when alkali fusibility phenol resin remains as it is, a well-known means may classify and what controlled molecular weight and molecular weight distribution may be used. As an approach of classifying in order to control molecular weight and molecular weight distribution, resin is ground, and solid liquid extraction is carried out by the organic solvent with suitable solubility, or resin is dissolved in a good solvent, and it is dropped into a poor solvent, or a poor solvent is dropped, and **-liquid or the approach of carrying out liquid-liquid extraction is mentioned.

[0016] (b) The sensitization agent used in sensitization agent this invention will not be especially limited, if it is the quinone diazide sulfonate of the polyhydroxy compound shown by said general formula (I). For example, 1, a 2-benzoquinone diazido-4-sulfonate, 1, a 2-naphthoquinonediazide-4-sulfonate, 1, a 2-naphthoquinonediazide-5-sulfonate, 2, a 1-naphthoquinonediazide-4-sulfonate, 2, a 1-naphthoquinonediazide-5-sulfonate, the sulfonate of other quinone diazide derivatives, etc. are mentioned.

[0017] The sensitization agent used by this invention is compoundable with the esterification reaction of the phenolic compound and quinone diazide sulfonic-acid compound which are shown by the general formula (I). As a quinone diazide sulfonic-acid compound, o-quinone diazide sulfonic-acid compounds, such as a 1, 2-benzoquinone diazido-4-sulfonic-acid, 1, 2-naphthoquinonediazide-4-sulfonic-acid,

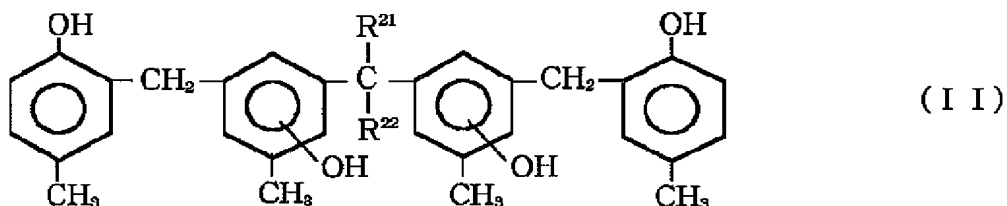
1, 2-naphthoquinonediazide-5-sulfonic-acid, 2, 1-naphthoquinonediazide-4-sulfonic-acid, 2, and 1-naphthoquinonediazide-5-sulfonic acid, other quinone diazide sulfonic-acid derivatives, etc. are mentioned, for example.

[0018] The quinone diazide sulfonate used by this invention makes a quinone diazide sulfonic-acid compound sulfonyl chloride by the chlorosulfonic acid according to a conventional method, and is obtained by carrying out the condensation reaction of the obtained quinone diazide sulfonylchloride and the polyhydroxy compound shown by the general formula (I). For example, a quinone diazide sulfonate can be prepared by dissolving the specified quantity of a polyhydroxy compound and 1 and 2-naphthoquinonediazide-5-sulfonyl chloride in solvents, such as dioxane, an acetone, or a tetrahydrofuran, adding the basic catalyst of triethylamine, a pyridine, a sodium carbonate, a sodium hydrogencarbonate, a sodium hydroxide, or a potassium hydroxide, making it react, rinsing the obtained product and drying.

[0019] The polyhydroxy compound used as the mother nucleus of a sensitization agent used by this invention is a compound shown by said general formula (I). In a general formula (I), chlorine and a bromine are desirable as a halogen atom. As an alkyl group, the alkyl group of carbon numbers 1-4 is desirable. As an alkenyl radical, the alkenyl radical of carbon numbers 2-5 is desirable. As an alkoxy group, the alkoxy group of carbon numbers 1-6 is desirable. As an aryl group, the aryl group of carbon numbers 6-15 is desirable. As a permutation aryl group, the aryl group permuted by the alkyl group and halogen atom of carbon numbers 1-4 is desirable. Moreover, as a polyhydroxy compound expressed with a general formula (I), the compound expressed with the following general formula (II) is desirable.

[0020]

[Formula 25]

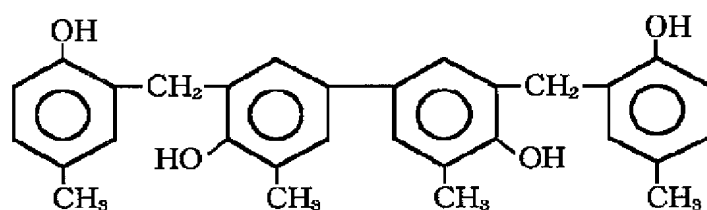


R21-R22: -- it is a hydrogen atom or an alkyl group, and respectively the same -- or it may be different from each other. As an alkyl group, the alkyl group of carbon numbers 1-4 is desirable as described above. As an example of the polyhydroxy compound shown by the general formula (I) used as the mother nucleus of a

sensitization agent used by this invention, the following compound (b-1) – (b-34) can be mentioned.

[0021]

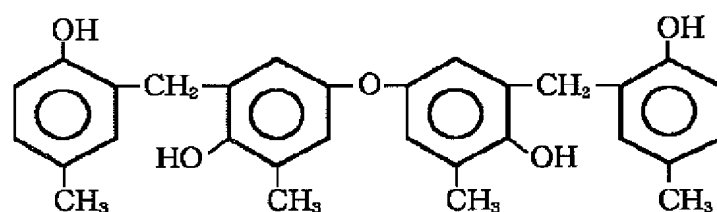
[Formula 26]



(b-1)

[0022]

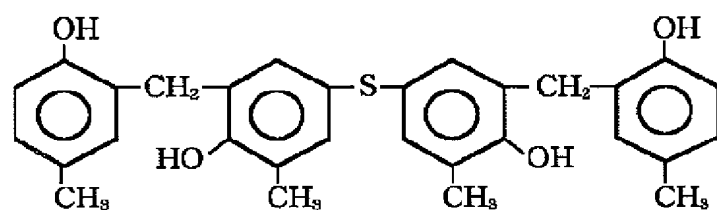
[Formula 27]



(b-2)

[0023]

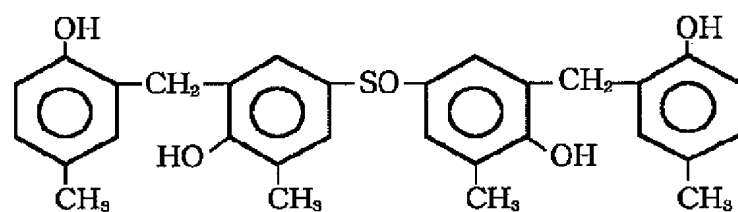
[Formula 28]



(b-3)

[0024]

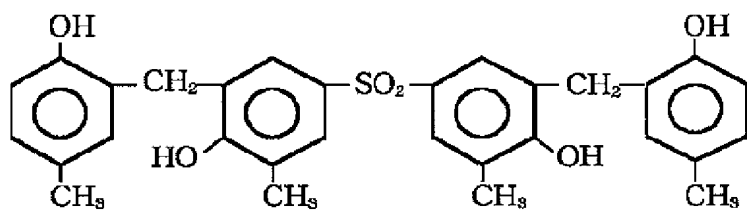
[Formula 29]



(b-4)

[0025]

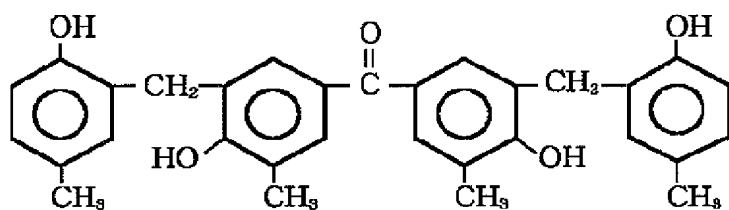
[Formula 30]



(b-5)

[0026]

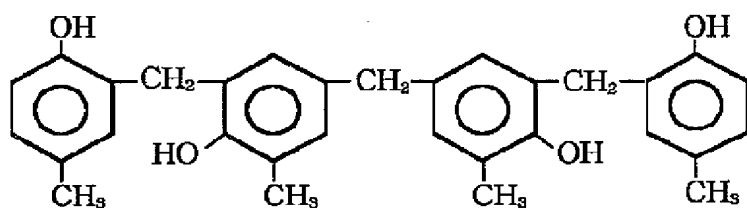
[Formula 31]



(b-6)

[0027]

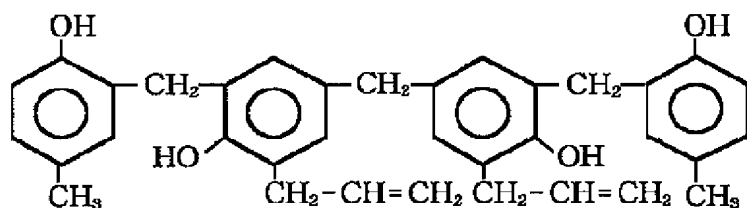
[Formula 32]



(b-7)

[0028]

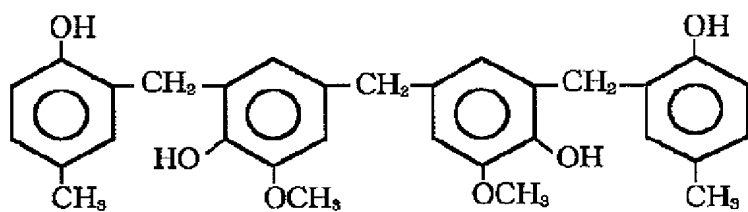
[Formula 33]



(b-8)

[0029]

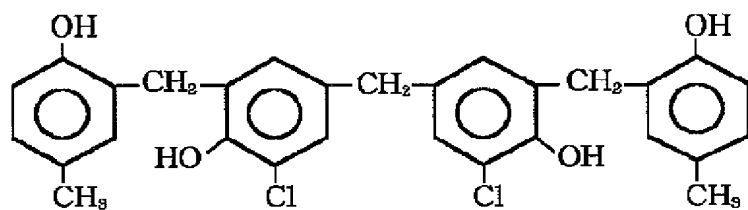
[Formula 34]



(b-9)

[0030]

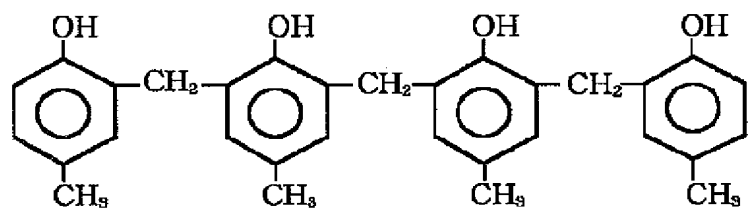
[Formula 35]



(b-10)

[0031]

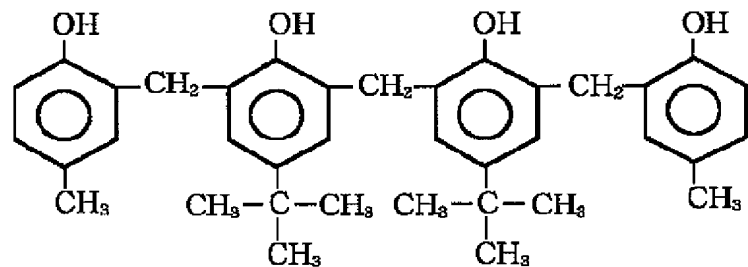
[Formula 36]



(b-11)

[0032]

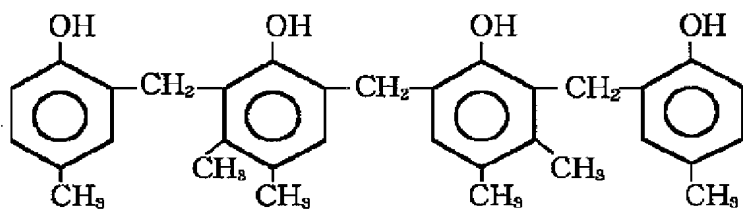
[Formula 37]



(b-12)

[0033]

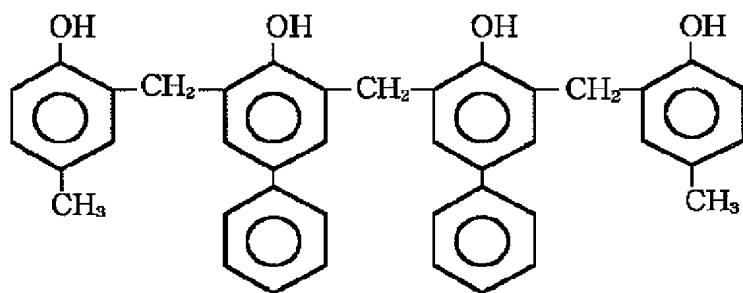
[Formula 38]



(b-13)

[0034]

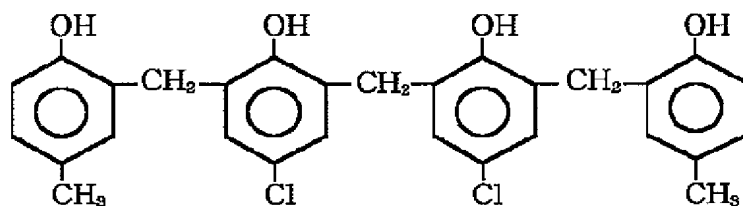
[Formula 39]



(b-14)

[0035]

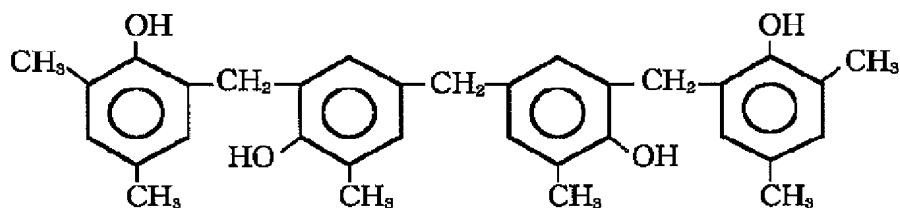
[Formula 40]



(b-15)

[0036]

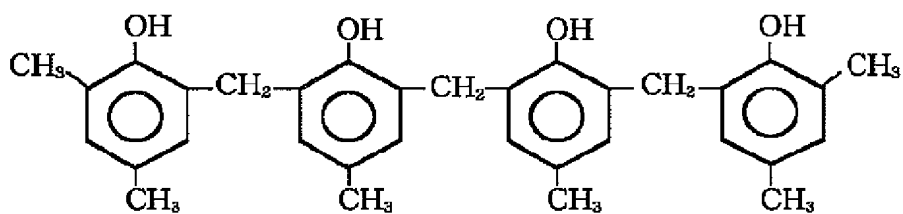
[Formula 41]



(b-16)

[0037]

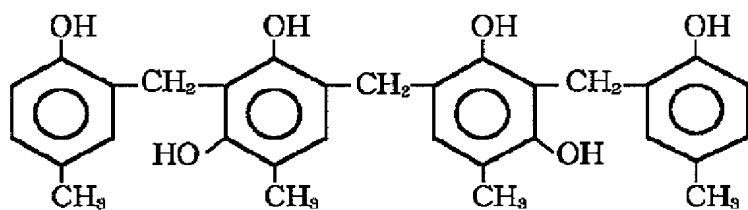
[Formula 42]



(b-17)

[0038]

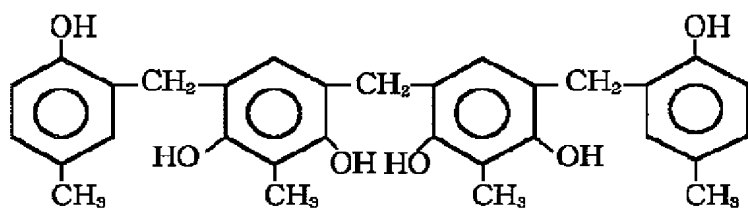
[Formula 43]



(b-18)

[0039]

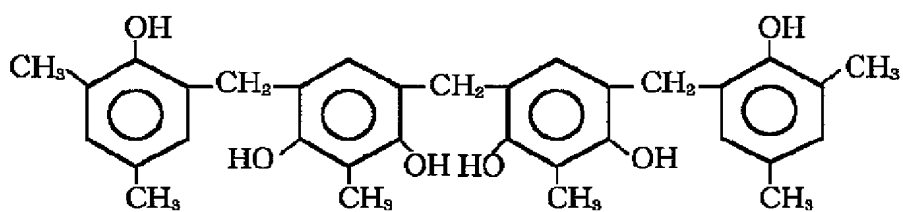
[Formula 44]



(b-19)

[0040]

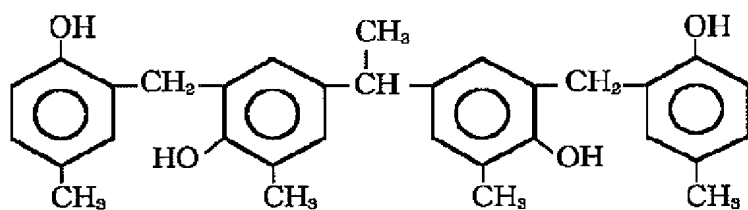
[Formula 45]



(b-20)

[0041]

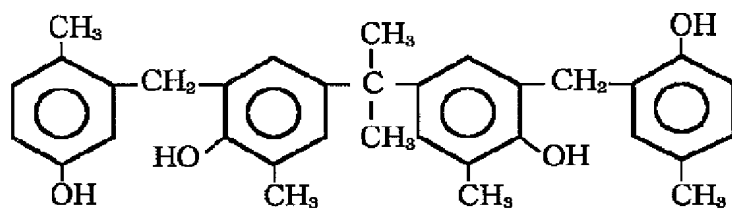
[Formula 46]



(b-21)

[0042]

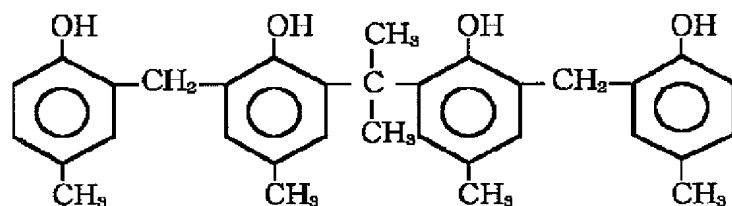
[Formula 47]



(b-22)

[0043]

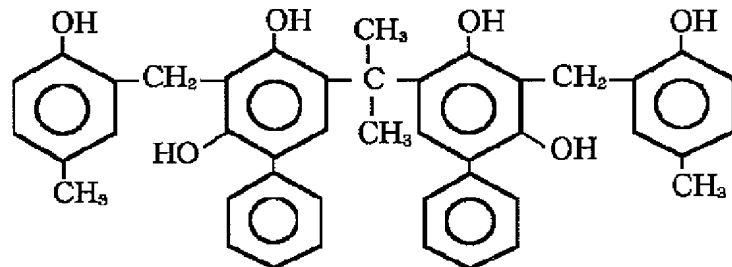
[Formula 48]



(b-23)

[0044]

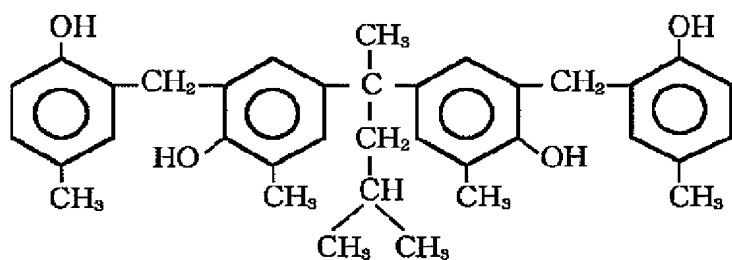
[Formula 49]



(b-24)

[0045]

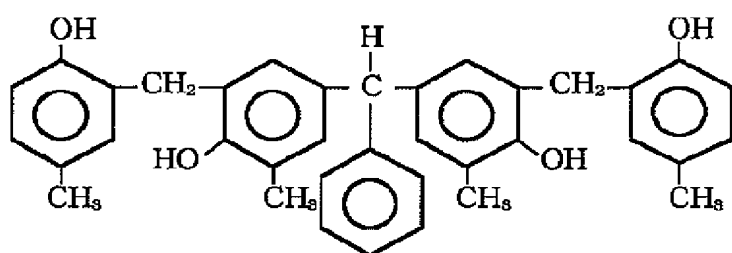
[Formula 50]



(b-25)

[0046]

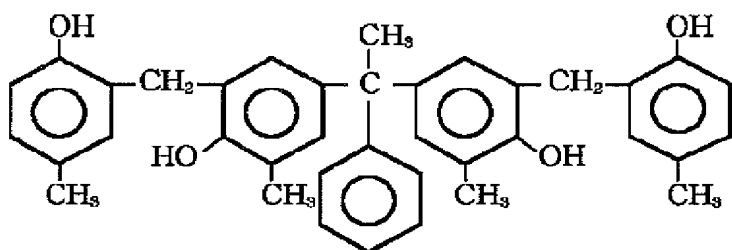
[Formula 51]



(b-26)

[0047]

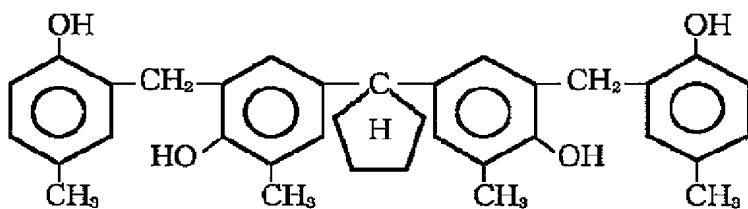
[Formula 52]



(b-27)

[0048]

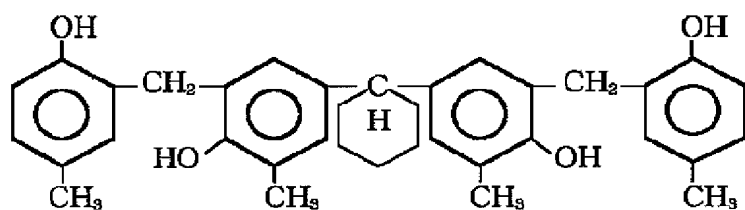
[Formula 53]



(b-28)

[0049]

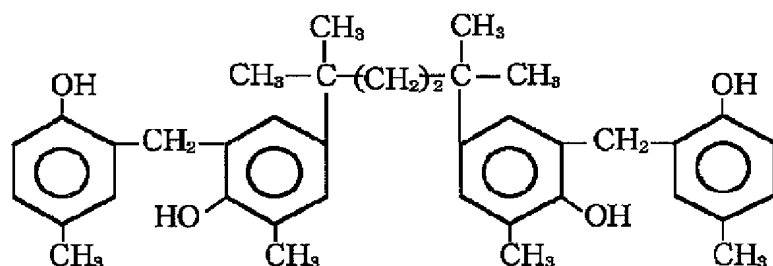
[Formula 54]



(b-29)

[0050]

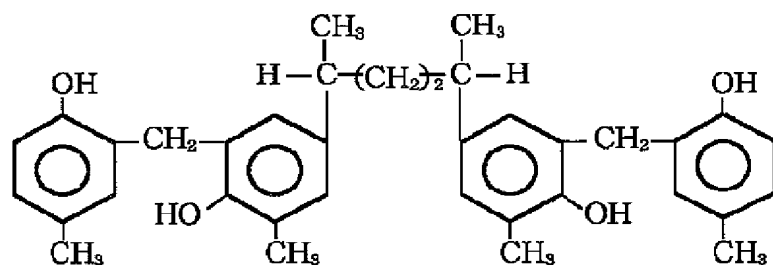
[Formula 55]



(b-30)

[0051]

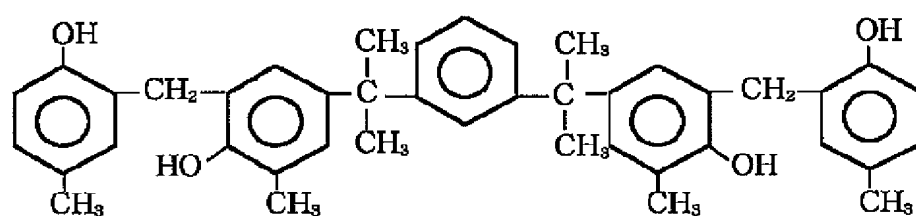
[Formula 56]



(b-31)

[0052]

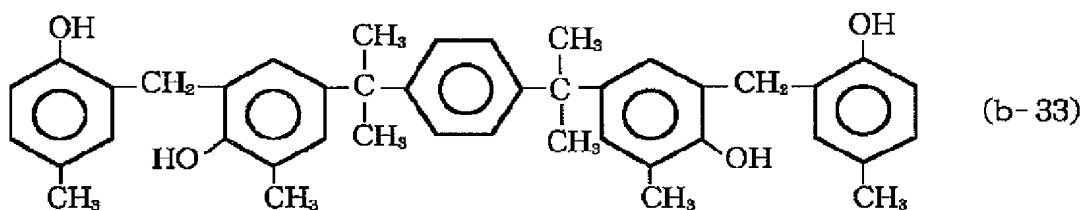
[Formula 57]



(b-32)

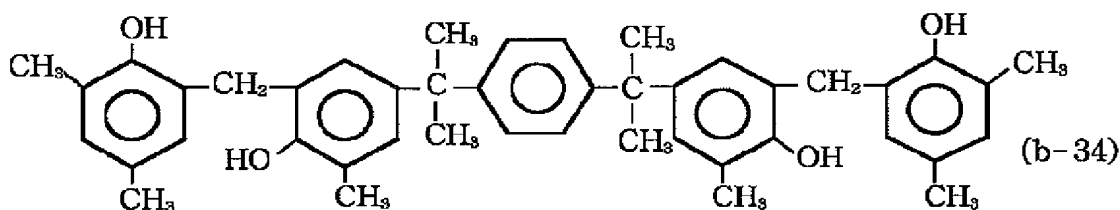
[0053]

[Formula 58]



[0054]

[Formula 59]



[0055] In the sensitization agent used by this invention, although especially the ratio (rate of average esterification) of esterification of the quinone diazide sulfonic-acid compound to the polyhydroxy compound shown by said general formula (I) is not limited, the OH radical of a phenolic compound is usually 65 – 90% of range more preferably 50 to 95% 20 to 100% (it writes as mol% of a quinone diazide sulfonic-acid compound to an OH radical). If the ratio of esterification is too low, degradation of a pattern configuration or definition will be imitated and it will come, and when the ratio of esterification is too high, degradation of sensibility is imitated and there is a ** case.

[0056] although especially the blending ratio of coal of the sensitization agent used by this invention is not what is limited — the alkali fusibility phenol resin 100 weight section — receiving — usually — the 1 – 100 weight section — desirable — 3 – 50 weight section — it is 10 – 40 weight section more preferably. If there is too little this blending ratio of coal, sufficient remaining rate of membrane will not be obtained, but degradation of definition is imitated and it comes, and conversely, if there is too much blending ratio of coal, heat-resistant degradation is imitated, and it comes and is not desirable. The sensitization agent used by this invention is independent, respectively, or can be used combining two or more sorts. Moreover, it can mix with small quantity (30 or less % of the weight [Usually] of the sensitization agent whole quantity) within limits which do not spoil the purpose of this invention, and the sensitization agent of another class can also be used for them. Especially as a sensitization agent of another class to mix, it is not limited, and if it is a well-known quinone diazide sulfonate, it can be used.

[0057] (c) Blend an aromatic compound (it may only be called a phenolic compound) with phenol nature hydroxyl with the positive-resist constituent of aromatic compound this invention with phenol nature hydroxyl. By blending a phenolic compound, the alkali solubility of alkali fusibility phenol resin can be promoted, and the sensibility of a positive-resist constituent, a remaining rate of membrane, resolution, thermal resistance, etc. can be raised. Although it will not be limited especially if it is an aromatic compound with phenol nature hydroxyl as a phenolic compound used by this invention, the aromatic compound shown by a following general formula (III) and/or a following general formula (IV) is desirable.

[0058]

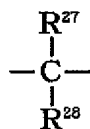
[Formula 60]



R23-R26: -- it is a hydrogen atom, a halogen atom, hydroxyl, an alkyl group, an alkenyl radical, an aryl group, or an alkoxy group, and respectively the same -- or it may be different from each other.

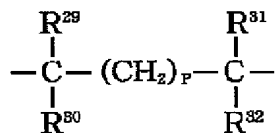
Y: Single bond, -O-, -S-, -SO-, -SO2-, -CO-, -CO2-, cyclo pen dust DIN, cyclohexylidene, phenylene, [0059]

[Formula 61]



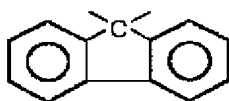
(-- R27 and R28: -- it is a hydrogen atom, an alkyl group, an alkenyl radical, an aryl group, or a permutation aryl group, and respectively the same -- or it may be different from each other. [] -- 0060]

[Formula 62]



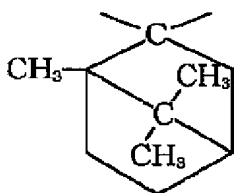
R29-R32: -- it is a hydrogen atom or an alkyl group, and respectively the same -- or it may be different from each other. p: It is the integer of 1-5. [0061]

[Formula 63]



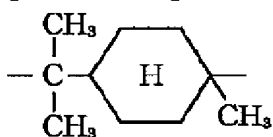
[0062]

[Formula 64]



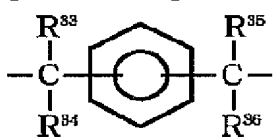
[0063]

[Formula 65]



Or [0064]

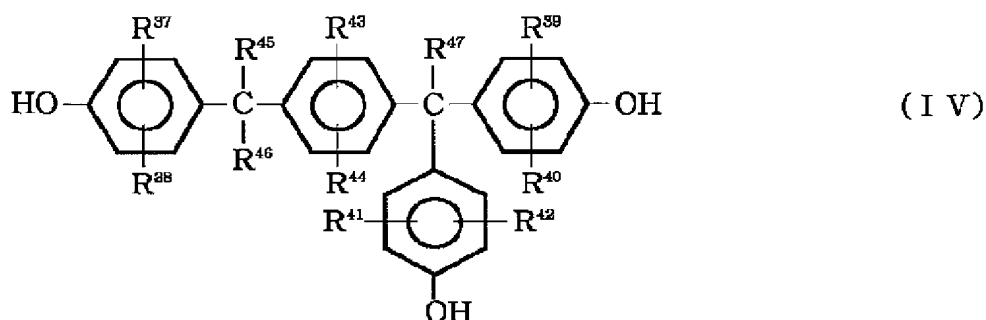
[Formula 66]



(--- R33-R36: --- it is a hydrogen atom or an alkyl group, and respectively the same --- or it may be different from each other.) --- from --- it is the becoming connection radical.

[0065]

[Formula 67]



R37-R42: --- it is a hydrogen atom, a halogen atom, hydroxyl, an alkyl group, an alkenyl radical, an aryl group, or an alkoxy group, and respectively the same --- or it may be different from each other.

R43 and R44: --- it is a hydrogen atom, a halogen atom, or an alkyl group, and respectively the same --- or it may be different from each other.

R45-R47: --- it is a hydrogen atom or an alkyl group, and respectively the same --- or it may be different from each other.

[0066] In the above-mentioned general formula (III) and (IV), chlorine and a bromine are desirable as a halogen atom. As an alkyl group, the alkyl group of carbon numbers 1-4 is desirable. As an alkenyl radical, the alkenyl radical of carbon numbers 2-5 is desirable. As an alkoxy group, the alkoxy group of carbon numbers 1-6 is desirable. As an aryl group, the aryl group of carbon numbers 6-15 is desirable. As a permutation aryl group, the aryl group permuted by the alkyl group and halogen atom of carbon numbers 1-4 is desirable. As an example of the aromatic compound shown by the general formula (III), the following compound (c-1) - (c-62) can be mentioned.

[0067]

[Formula 68]



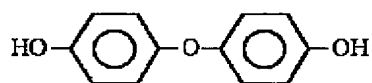
[0068]

[Formula 69]



[0069]

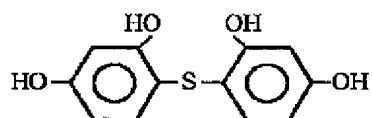
[Formula 70]



(C-3)

[0070]

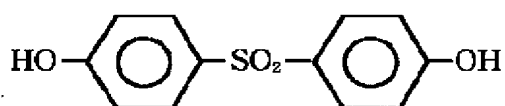
[Formula 71]



(C-4)

[0071]

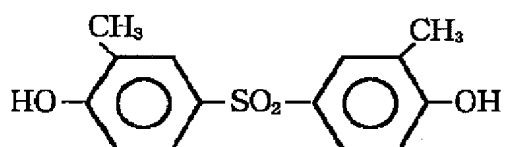
[Formula 72]



(C-5)

[0072]

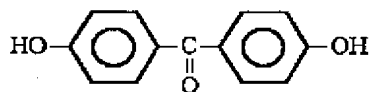
[Formula 73]



(C-6)

[0073]

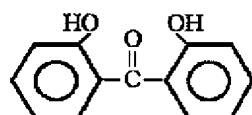
[Formula 74]



(C-7)

[0074]

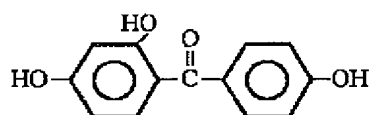
[Formula 75]



(C-8)

[0075]

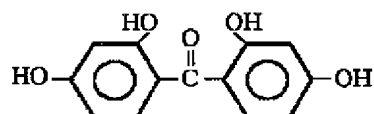
[Formula 76]



(C-9)

[0076]

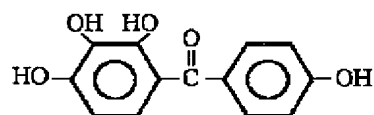
[Formula 77]



(C-10)

[0077]

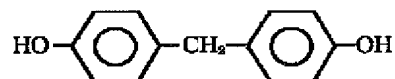
[Formula 78]



(C-11)

[0078]

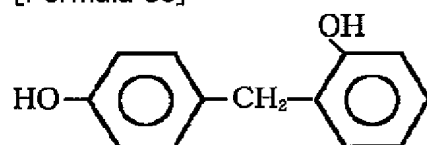
[Formula 79]



(C-12)

[0079]

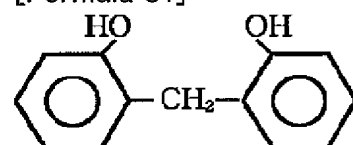
[Formula 80]



(C-13)

[0080]

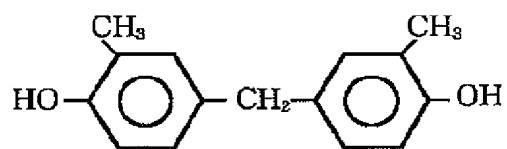
[Formula 81]



(C-14)

[0081]

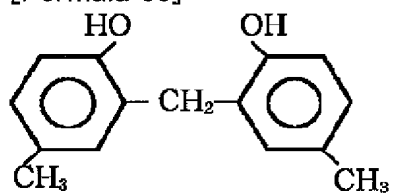
[Formula 82]



(C-15)

[0082]

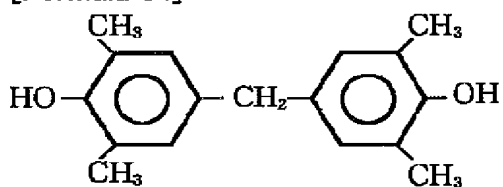
[Formula 83]



(C-16)

[0083]

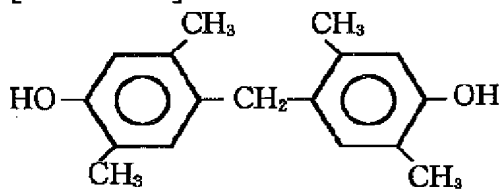
[Formula 84]



(C-17)

[0084]

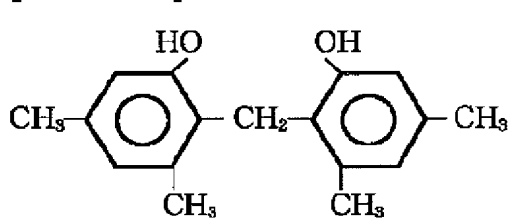
[Formula 85]



(C-18)

[0085]

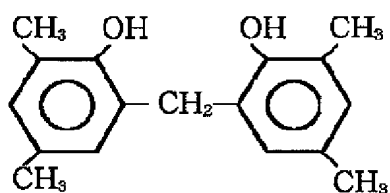
[Formula 86]



(C-19)

[0086]

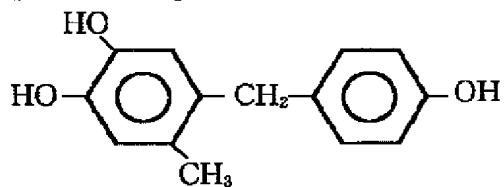
[Formula 87]



(C-20)

[0087]

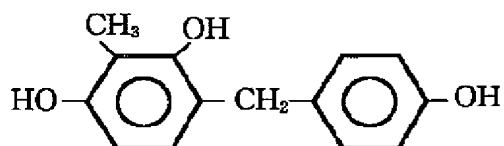
[Formula 88]



(C-21)

[0088]

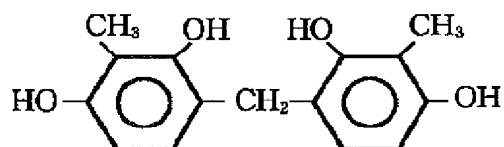
[Formula 89]



(C-22)

[0089]

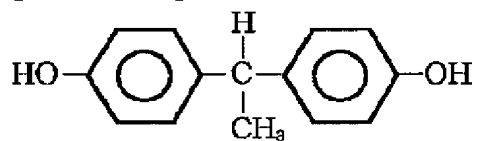
[Formula 90]



(C-23)

[0090]

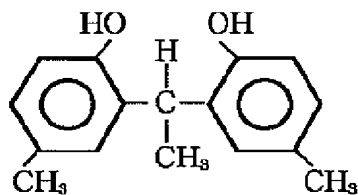
[Formula 91]



(C-24)

[0091]

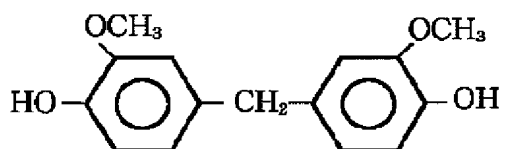
[Formula 92]



(C-25)

[0092]

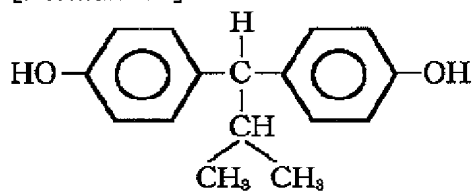
[Formula 93]



(C-26)

[0093]

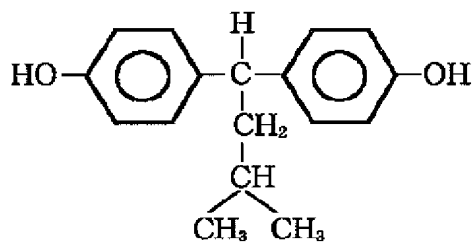
[Formula 94]



(C-27)

[0094]

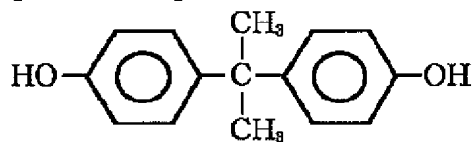
[Formula 95]



(C-28)

[0095]

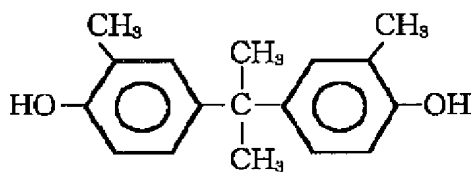
[Formula 96]



(C-29)

[0096]

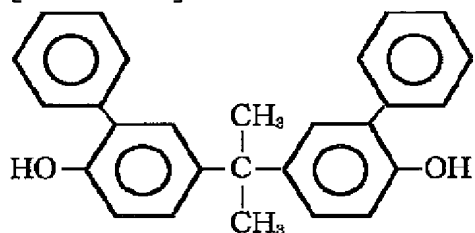
[Formula 97]



(C-30)

[0097]

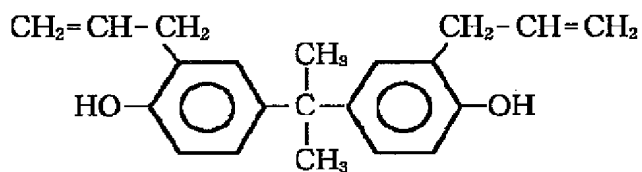
[Formula 98]



(C-31)

[0098]

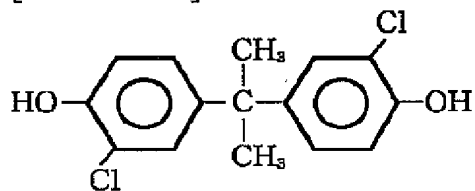
[Formula 99]



(C-32)

[0099]

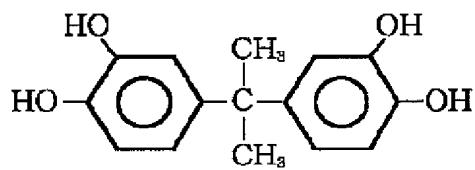
[Formula 100]



(C-33)

[0100]

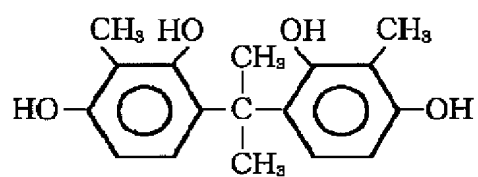
[Formula 101]



(C-34)

[0101]

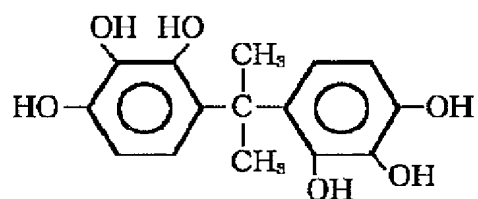
[Formula 102]



(C-35)

[0102]

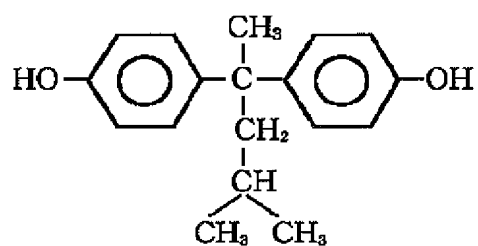
[Formula 103]



(C-36)

[0103]

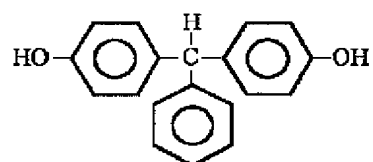
[Formula 104]



(C-37)

[0104]

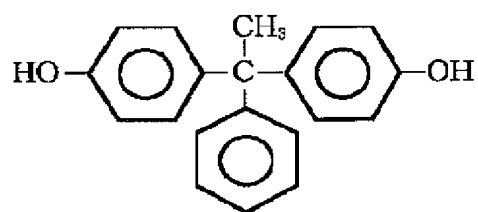
[Formula 105]



(C-38)

[0105]

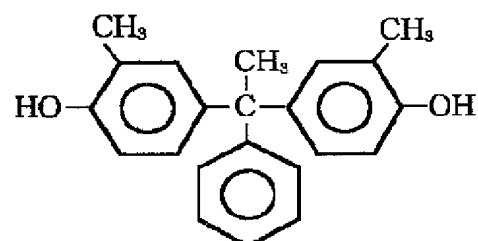
[Formula 106]



(C-39)

[0106]

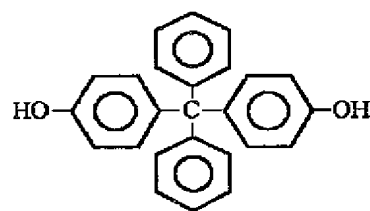
[Formula 107]



(C-40)

[0107]

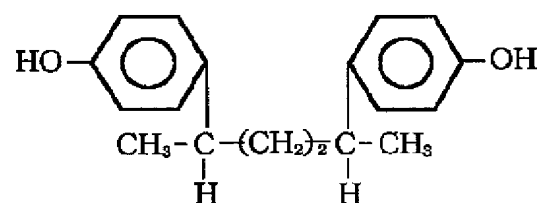
[Formula 108]



(C-41)

[0108]

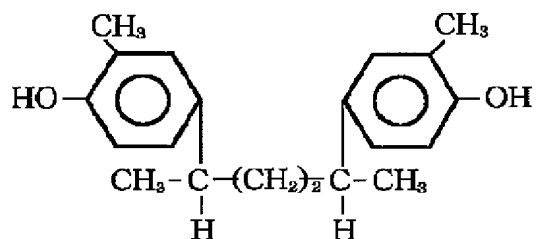
[Formula 109]



(C-42)

[0109]

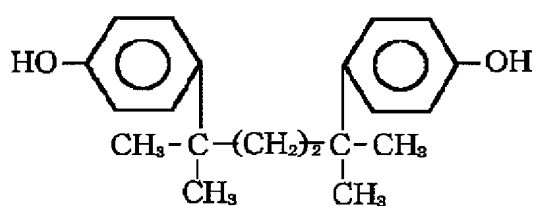
[Formula 110]



(C-43)

[0110]

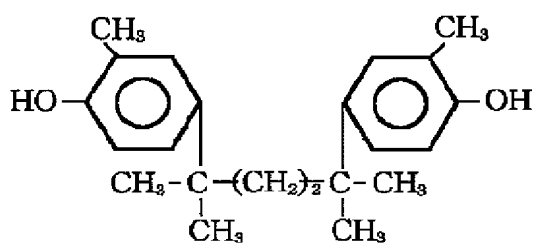
[Formula 111]



(C-44)

[0111]

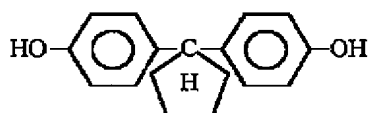
[Formula 112]



(C-45)

[0112]

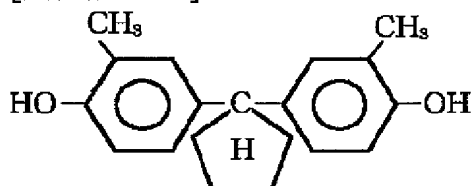
[Formula 113]



(C-46)

[0113]

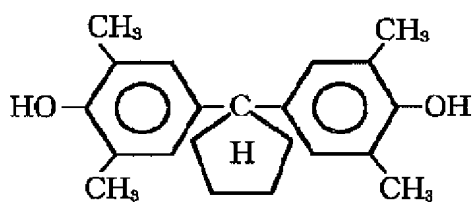
[Formula 114]



(C-47)

[0114]

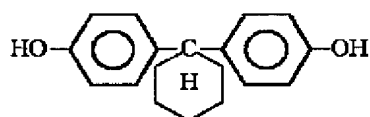
[Formula 115]



(C-48)

[0115]

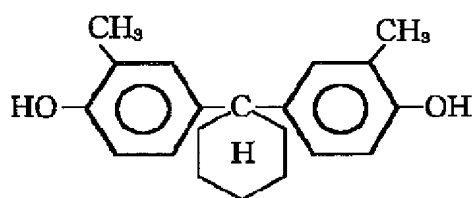
[Formula 116]



(C-49)

[0116]

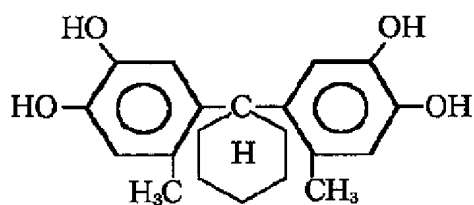
[Formula 117]



(C-50)

[0117]

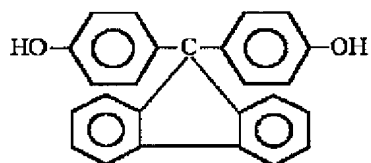
[Formula 118]



(C-51)

[0118]

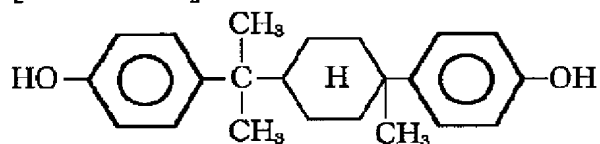
[Formula 119]



(C-52)

[0119]

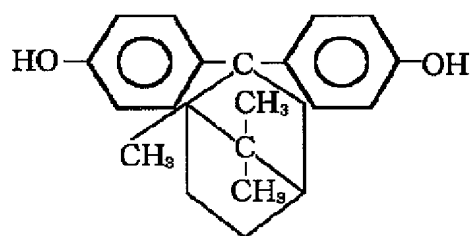
[Formula 120]



(C-53)

[0120]

[Formula 121]



(C-54)

[0121]

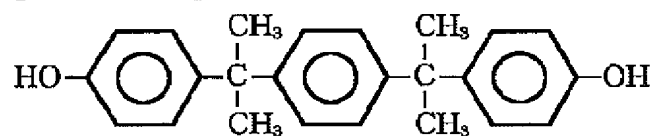
[Formula 122]



(C-55)

[0122]

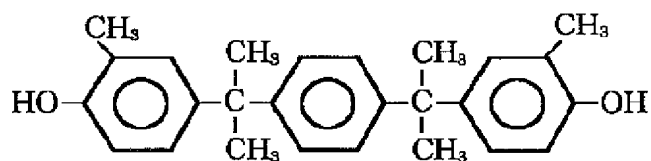
[Formula 123]



(C-56)

[0123]

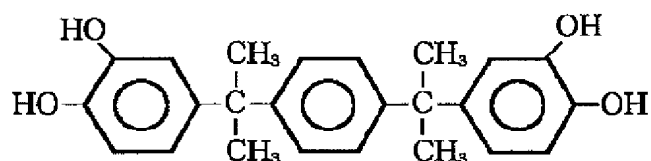
[Formula 124]



(C-57)

[0124]

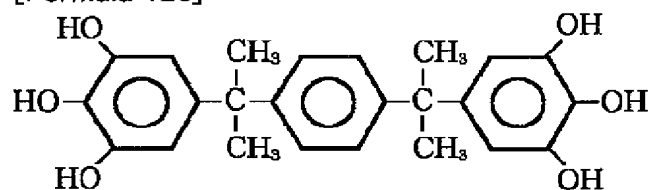
[Formula 125]



(C-58)

[0125]

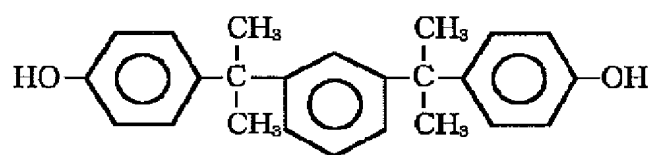
[Formula 126]



(C-59)

[0126]

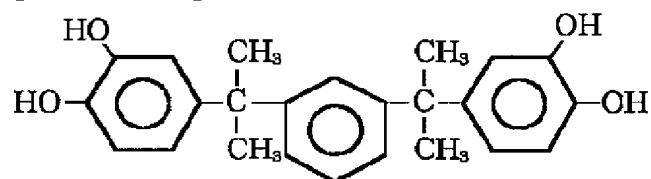
[Formula 127]



(C-60)

[0127]

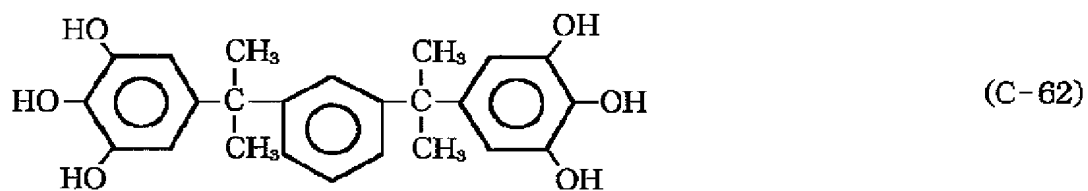
[Formula 128]



(C-61)

[0128]

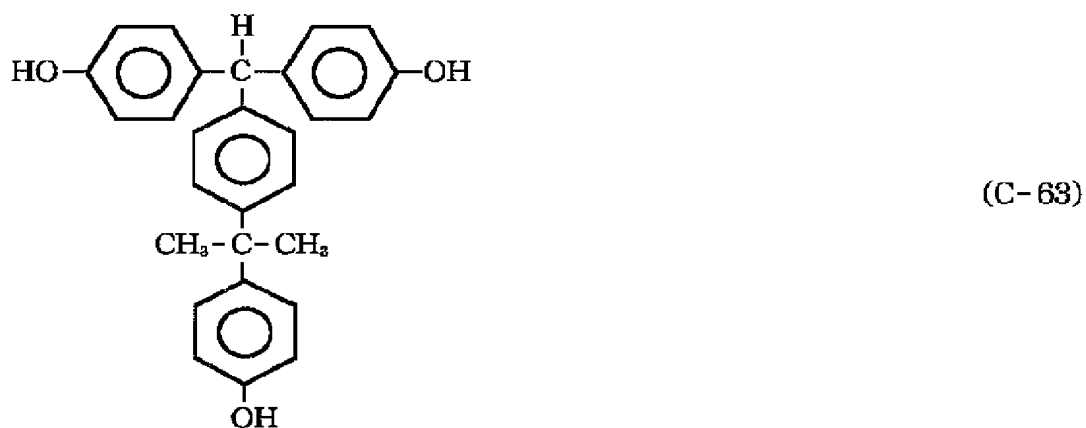
[Formula 129]



As an example of the aromatic compound shown by the general formula (IV), the following compound (c-63) - (c-66) can be mentioned.

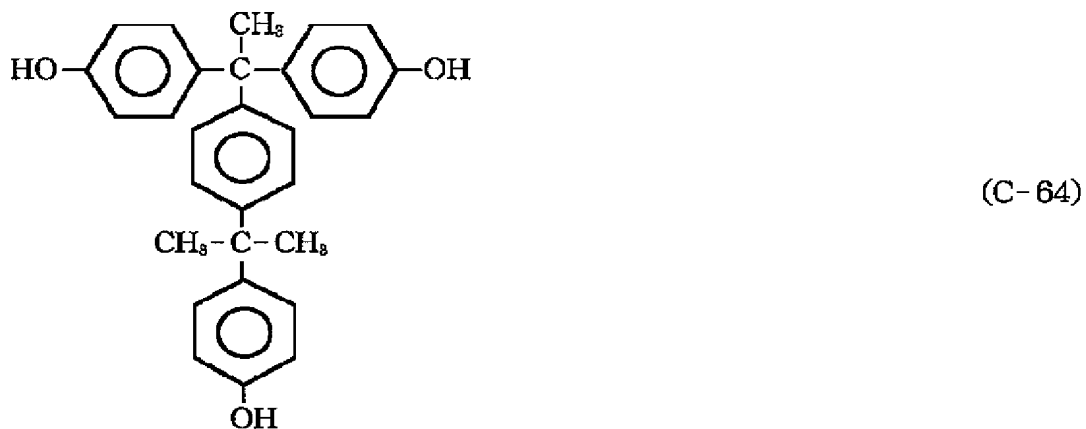
[0129]

[Formula 130]



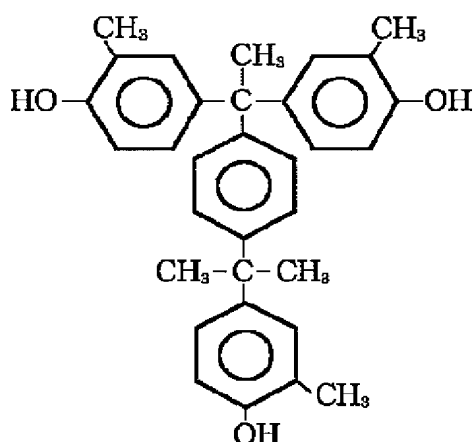
[0130]

[Formula 131]



[0131]

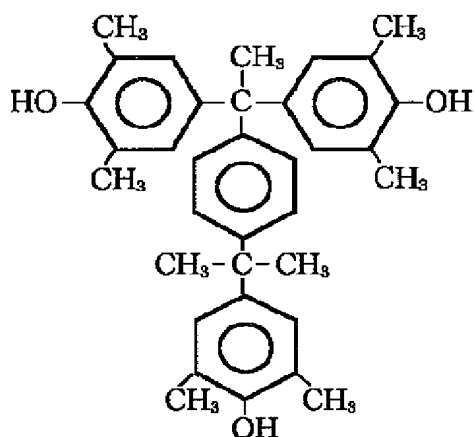
[Formula 132]



(C-65)

[0132]

[Formula 133]



(C-66)

[0133] Also in these phenolic compounds, especially the compound of c-1, c-12, c-13, c-14, c-49, c-52, c-56, c-60, and c-64 is desirable. The blending ratio of coal of these phenolic compounds is usually the 1 - 100 weight section to the alkali fusibility phenol resin 100 weight section. Although the desirable blending ratio of coal of a phenolic compound changes with classes, the blending ratio of coal, etc. of the presentation of alkali fusibility phenol resin, molecular weight, molecular weight distribution, or a sensitization agent, it is 3 - 60 weight section in general. Moreover, these phenolic compounds are independent, respectively, or can be used combining two or more sorts.

[0134] The positive-resist constituent of solvent this invention is usually dissolved and used for a solvent, in order to apply to a substrate and to form the resist film. As a solvent, an acetone, a methyl ethyl ketone, a cyclohexanone, Ketones, such as

cyclopentanone and 2-heptanone; N-propyl alcohol, Alcohols, such as iso-propyl alcohol, n-butyl alcohol, and a cyclohexanol; Ethylene glycol wood ether, Ether, such as ethylene glycol diethylether and dioxane; Ethylene glycol monomethyl ether, Alcoholic ether, such as ethylene glycol monoethyl ether; Formic-acid propyl, Formic-acid butyl, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, Ester, such as methyl butyrate and ethyl butylate; 2-hydroxypropanoic acid methyl, 2-hydroxypropanoic acid ethyl, 2-methoxy methyl propionate, 2-methoxy ethyl propionate, 2-ethoxy methyl propionate, Mono-hydroxy acid ester, such as 2-ethoxy ethyl propionate; A cellosolve acetate, Methyl-cellosolve acetate, ethylcellosolve acetate, a propyl cellosolve acetate, Cellosolve ester, such as butyl-cellosolve acetate; Propylene glycol, Propylene glycol monomethyl ether, PUORENGURIKORU monomethyl ether acetate, Propylene glycols, such as propylene glycol monoethyl ether acetate and the propylene glycol monobutyl ether; The diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, Halogenated hydrocarbon [, such as a diethylene-glycols; trichloroethylene,], such as the diethylene-glycol JIECHIRU ether and the diethylene-glycol methylethyl ether; Toluene, Aromatic hydrocarbon, such as a xylene; polar solvents, such as dimethylacetamide, dimethylformamide, and N-methyl acetamide, etc. are mentioned. Independence or two sorts or more can be mixed and used for these solvents, respectively. These solvents are used in the amount which is sufficient for each component dissolving in homogeneity.

[0135] In the positive-resist constituent of other component this inventions, in order to improve development nature, preservation stability, thermal resistance, etc. if needed, a copolymer with styrene, an acrylic acid, a methacrylic acid, or a maleic anhydride, the copolymer of an alkene and a maleic anhydride, a vinyl alcohol polymer, a vinyl-pyrrolidone polymer, rosin, a shellac, etc. can be added. an addition -- the alkali fusibility phenol resin 100 weight section -- receiving -- the above-mentioned polymer 0 - 50 weight sections -- it is 5 - 20 weight section preferably. The positive-resist constituent of this invention can be made to contain an additive with the compatibility of a color, a surfactant, a preservation stabilizer, a sensitizer, a striae SHON inhibitor, a plasticizer, etc. if needed.

[0136] As a developer of the positive-resist constituent of developer this invention, although the water solution of alkali is used Specifically A sodium hydroxide, a potassium hydroxide, a sodium silicate, Inorganic alkali, such as ammonia; Primary-amines; diethylamines, such as ethylamine and propylamine, The second amines, such as a dipropyl amine; Tertiary-amines; dimethyl methanol amines, such as

a trimethylamine and triethylamine, Alcoholic amines, such as triethanolamine; Tetramethylammonium hydroxide, Quarternary ammonium salt, such as tetraethylammonium hydroxide, trimethyl hydroxymethyl ammonium hydroxide, triethyl hydroxymethyl ammonium hydroxide, and trimethylhydroxyethylammonium hydroxide, etc. is mentioned. Furthermore, optimum dose addition of water-soluble organic solvents, such as a methanol, ethanol, propanol, and ethylene glycol, a surfactant, a preservation stabilizer, the dissolution inhibitor of resin, etc. can be carried out at the above-mentioned alkali water solution if needed.

[0137]

[Example] An example and the example of a comparison are given to below, and this invention is explained to it still more concretely. In addition, the section and % are weight criteria as long as there is no notice especially. The resist evaluation approach in the following examples and examples of a comparison is as follows.

- (1) Express with the exposure time (msec) the amount of exposure energy which a 1:1 line & tooth space with a sensibility of 0.60 micrometers can form as a design dimension.
- (2) Express the critical resolution (micrometer) in the resolution above-mentioned exposure conditions.
- (3) Express the ratio (%) of the resist film before and behind remaining-rate-of-membrane development.
- (4) The wafer in which the pattern configuration resist pattern was formed was cut from the perpendicular direction of the Rhine pattern, and the result observed with the electron microscope from the direction of a cross section of a pattern was shown. The sidewall of a pattern has started at the include angle of 80 degrees or more to the substrate, and the thing without film decrease was judged to be "fitness." The sidewall judged what has started at the include angle of less than 80 degrees to be a "taper." The thing with a little film decreases was made into "film decrease smallness", and the large thing was made into "film decrease size."

[0138] [The synthetic example 1] (composition of novolak resin A-1)

m-cresol 385g, 315g [of p-cresol], and 37% formalin 360g and 2.49g of oxalic acid 2 hydrates are taught, and it was made to react to the flask equipped with a cooling pipe and stirring equipment for 2 hours, keeping at 95-100 degrees C. Then, after decompressing to 10 - 30mmHg and removing an unreacted monomer and water, having carried out distillation removal of the water over 2 hours, and carrying out a temperature up to 180 more degrees C at 100-105 degrees C, melting resin was returned and collected to the room temperature, and 515g (A-1) of novolak resin was

obtained. The weight average molecular weight of the polystyrene conversion by the gel permeation chromatography (GPC) of this novolak resin was 7000.

[0139] [The synthetic example 2] (composition of novolak resin A-2)

Ethylcellosolve acetate 360g was added to 380g of novolak resin obtained in the synthetic example 1, and it dissolved in it. The flask was equipped with the tap funnel, where temperature is controlled at 80–85 degrees C, toluene 950g was dropped from the tap funnel, and it heated at 80 more degrees C for 1 hour. To the room temperature, it cooled slowly and put for further 1 hour. After the decantation removed the supernatant of a pitch which has deposited, 570g (2-hydroxypropanoic acid ethyl) of ethyl lactates was added, it heated at 100 degrees C by 100mmHg, residual toluene was removed, and the ethyl lactate solution of novolak resin (A-2) was obtained. The weight average molecular weight of the polystyrene conversion by GPC of this novolak resin was 12100.

[0140] [The synthetic example 3] (composition of the sensitization agent B-1)

1 of amount equivalent to 70–mol% of this OH radical and 2-naphthoquinonediazide-5-sulfonic-acid chloride was dissolved in dioxane, using the compound of said formula (b-7) as a polyhydroxy compound, and it considered as 10% of solution. Controlling temperature at 20–25 degrees C, the triethylamine for 1.2Eq of 1 and 2-naphthoquinonediazide-5-sulfonic-acid chloride was dropped over 30 minutes, it held for further 2 hours, and the reaction was completed. the solid content which has deposited — filtration — it ion-exchange-water-washed, dried and the sensitization agent (B-1) was obtained.

[0141] [The synthetic example 4] (composition of the sensitization agent B-2 to B-8)

According to the same formula as the synthetic example 3, the sensitization agent (B-2 to B-8) was compounded except having changed the preparation mole ratio of 1 and 2-naphthoquinonediazide-5-sulfonic-acid chloride to the class or the number of OH radicals of a polyhydroxy compound. The class and preparation mole ratio of a polyhydroxy compound were shown in Table 1.

[0142] [The synthetic example 5] (composition of the sensitization agent B-9)

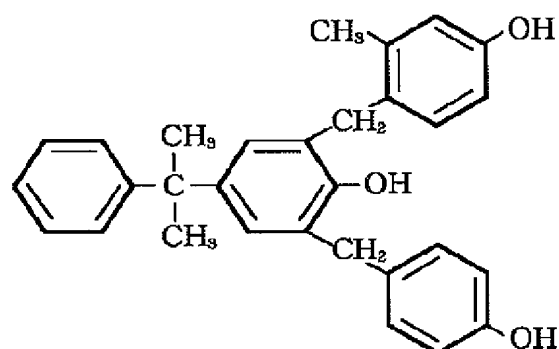
The sensitization agent (B-9) was compounded by the same formula as the synthetic example 3 except having made 85% the preparation mole ratio of 1 and 2-naphthoquinonediazide-5-sulfonic-acid chloride to this OH radical, using a 2, 3, 4, and 4'-tetra-hydroxy benzophenone as a polyhydroxy compound.

[0143] The sensitization agent (B-10) was compounded by the same formula as the synthetic example 3 using the compound (d-1) expressed with the following chemical formula as a [synthetic example 6] polyhydroxy compound except having made 80%

the preparation mole ratio of 1 and 2-naphthoquinonediazide-5-sulfonic-acid chloride to this OH radical.

[0144]

[Formula 134]



(d-1)

[0145]

[Table 1]

感光剤	対ヒドロキシ化合物の種類	対ヒドロキシ化合物の水酸基に対する 1,2-ナフトキノンジアゾ-5-スルホン酸クロライド の仕込比 (wt%)
B-1	b-7	70
B-2	b-7	75
B-3	b-1	80
B-4	b-11	75
B-5	b-16	65
B-6	b-19	80
B-7	b-22	75
B-8	b-27	65
B-9	2,3,4,4'-テトラヒドロキシベンゾフェノン	85
B-10	d-1	80

[0146] The aromatic compound (phenolic compound) with the alkali fusibility phenol resin (novolak resin), the sensitization agent, and phenol nature hydroxyl of the presentation shown in the [examples 1-14] table 2 was dissolved in the ethyl lactate (2-hydroxypropanoic acid ethyl) solvent, and solvent loadings were adjusted so that it could apply to 1.17-micrometer thickness. These solutions were filtered with the filter made from polytetrafluoroethylene fluoro ethylene of 0.1 micrometers of apertures (PTFE filter), and the resist solution was prepared.

[0147] After applying the above-mentioned resist solution by the spin coater on a silicon wafer, it prebaked for 90 seconds with the 90-degree C hot plate, and the resist film of 1.17 micrometers of thickness was formed. The silicon wafer in which this resist film was formed was exposed using i line stepper NSR-1755i7A (the NIKON CORP. make, NA=0.50) and the reticle for a test, changing the exposure time. Next, after carrying out after [exposure] BEKU (Post Exposure Baking;PEB) of this wafer for 60 seconds with a 110-degree C hot plate, negatives were developed for 23 degrees C and 1 minute and with a paddle method in the tetramethylammonium hydroxide water solution 2.38%, and the positive type pattern was formed. The wafer with which this pattern was formed was taken out and sensibility, resolution, and a pattern configuration were observed with the electron microscope. The remaining rate of membrane measured and asked for the thickness before and behind development of the part in which a pattern is not formed on the wafer. These evaluation results are shown in Table 2.

[0148] Except having not used the [example 1 of comparison] phenolic compound, the resist solution was prepared like the example 1 and the same conditions estimated the resist. This result is shown in Table 2.

[0149] Using the sensitization agent B-9 which is a sensitization agent of [example 2 of comparison] this invention out of range, except having not used a phenolic compound, the resist solution was prepared like the example 1 and the same conditions estimated the resist. This result is shown in Table 2.

[0150] Using the sensitization agent B-10 which is a sensitization agent of [example 3 of comparison] this invention out of range, except having not used a phenolic compound, the resist solution was prepared like the example 1 and the same conditions estimated the resist. This result is shown in Table 2.

[0151]

[Table 2]

		ポジ型レジストの組成						評 価 結 果			
		樹脂 (a)		感光剤 (b)		7 α -H化合物 (c)		感 度 (msec)	残 膜 率 (%)	解 像 度 (μ m)	パ タ ー ン 形 状
		化 合 物	量 (部)	化 合 物	量 (部)	化 合 物	量 (部)				
実 施 例	1	A-1	95	B-1	30	C-64	5	420	99	0.38	良好
	2	A-2	80	B-2	30	C-49	20	440	100	0.36	良好
	3	A-2	80	B-3	30	C-49	20	480	100	0.38	良好
	4	A-2	80	B-4	30	C-49	20	480	100	0.36	良好
	5	A-2	80	B-5	30	C-49	20	420	100	0.36	良好
	6	A-2	80	B-6	26	C-49	20	400	100	0.38	良好
	7	A-2	80	B-7	30	C-49	20	460	100	0.36	良好
	8	A-2	80	B-8	30	C-49	20	480	100	0.38	良好
	9	A-2	80	B-2	30	C-1	20	400	100	0.36	良好
	10	A-2	80	B-2	30	C-13	20	440	100	0.36	良好
	11	A-2	80	B-2	30	C-52	20	380	100	0.36	良好
	12	A-2	80	B-2	30	C-56	20	400	100	0.36	良好
	13	A-2	80	B-2	30	C-60	20	420	100	0.36	良好
	14	A-2	80	B-2	30	C-12 C-49	10 10	400	100	0.36	良好
比 較 例	1	A-1	100	B-1	30	—	—	460	99	0.40	良好
	2	A-1	100	B-9	30	—	—	380	99	0.44	テーパー
	3	A-1	100	B-10	30	—	—	520	100	0.40	良好

[0152]

[Effect of the Invention] According to this invention, the positive-resist constituent excellent in many properties, such as sensibility, a remaining rate of membrane, definition, and a pattern configuration, can be offered. Especially the positive resist of this invention is suitable for micro processing 1 micrometer or less.

[Translation done.]